Comparison of the Forest Fertilizer Properties of the Ash Fraction from the Co-Firing of Peat and Forest Residues at a Large-Sized (246 MW) Combustion Plant of a Pulp and Paper Mill Complex

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Abstract

The bottom ash and fly ash investigated in this study originated from the bubbling fluidized bed boiler at the large-sized (246 MW) combustion plant of a pulp and paper mill complex. Approximately 40 % of the energy produced by the boiler originated from the incineration of commercial peat fuel, and approximately 60 % from the incineration of clean forest residues (*i.e.* bark, woodchip and sawdust). Due to the low heavy metal concentrations (As, Cd, Cr, Cu, Hg, Pb, Ni and Zn) in the bottom ash and fly ash, these residues are potential forest fertilizers as such. However, additional Ca is needed for the bottom ash, because its Ca concentration of 5.8 % (d.w.) was lower than the statutory Finnish minimum limit value of 6.0 % (d.w.) for Ca in forest fertilizers. Except for potassium, nutrients and heavy metals were enriched in the fly ash. Compared to the total phosphorous content, which was 0.2 % (d.w.) in the bottom ash and 1.3 % (d.w.) in the fly ash, the water soluble phosphorous content in both ashes was negligible (<0.01 %; d.w.). This finding is discussed on the basis of the minerals observed in the XRD data for the ashes, as well as on the grounds of findings reported by other researchers.

Keywords: Ash, fertilizer, fluidized bed boiler, forest residue, waste

INTRODUCTION

In Finland, large combustion plants (LCP) are found among condensing power plants, co-generation power plants for industry and district heating, and among the peaking heat-only boilers in district heat and industrial heat distribution systems. In these plants, the bubbling fluidized bed (BFB) boiler is the most common-ly used boiler type, since it is especially suitable for inhomogeneous fuels, even with high moisture contents, although circulating fluidized bed (CFB) boilers are also used. Co-firing of biomass such as peat with clean forest wood-based residues such as bark, wood chips and sawdust has been very successfully applied at many Finnish large combustion plants, especially in BFB boilers used by the forest indus-

try. This is because the processing of wood, which is the main raw material used in pulp and paper mills, wood handling plants, sawmills and groundwood mills generate a significant amount of wood-based residues such as bark, woodchips and sawdust, which have a calorific value and are therefore necessary to incinerate. Wood-based biomass can be considered as "CO_2-neutral". The amount of CO_2 released from the combustion of wood-based biomass sources is equivalent to that absorbed by plants in photosynthesis during their lifetime. Consequently, atmospheric CO_2 absorbed *via* photosynthesis is returned to the atmosphere during combustion. Thus, there is no net input of CO_2 into the atmosphere in the combustion of wood-based biomass [1]. Furthermore, when wood-based biomass is co-fired with peat, as it usually is in Finland, the wood ash may react with the sulphur from the peat and act as a desulphurising agent. From the perspective of environmental and atmospheric emissions, this is an advantage, since it prevents airborne pollution such as sulphur dioxide (SO_2) [2]. In this context, it is worth mentioning that according to European Union legislation, the utilization of the energy content of process residues is considered as a best available technique (BAT) in the pulp and paper industry [3, 4].

The extraction of forest harvest residues such as small trees, branches and tops has increased in a number of countries in recent decades. With such whole-tree harvesting, the export of nutrients and acid-buffering substances from the growing site is increased, potentially affecting tree growth and the chemistry of runoff water. There is consequently a long-term need for compensatory fertilization at many harvesting sites. Compensation is particularly important at sites with weak mineralogy, *e. g.* on organic soils, at severely acidified sites or sites exposed to high nitrogen deposition. During the combustion of peat and forest residues, acid-buffering substances as well as most nutrients are concentrated in the ash [5, 6]. Therefore, the recycling of the nutrients contained in ash, now mostly disposed of as waste, could be an interesting alternative for improving the nutritional status of forest soils. The large and increasing volume of ash residues arising from Finnish pulp and paper mills

is motivating a search for alternative disposal options to landfill. The utilization of solid wastes and residues, such as ash, allows industry to implement the 3R principle of the reduction, reuse and recycling of materials as beneficial products [7]. Although the pulp and paper mill industry has long traditions in environmental protection, and the importance of disposal options other than that of landfilling was already recognized in the mid 1950s [8], there is evidently increasing pressure for the further utilization of industrial residues and wastes such as ash residues in pulp and paper mills. This is because of the large and increasing volumes of ash residues arising from Finnish pulp and paper mills. Increasing costs of landfill disposal, difficulties in acquiring new sites for disposal and the development of environmental management systems are driving forces in minimizing the amount of solid wastes arising for disposal [9].

EXPERIMENTAL

Bottom and fly ash sampling

The bottom ash and fly ash investigated in this study originated from the large-sized (246 MW) combustion plant of a pulp and paper mill complex. This combustion plant uses a bubbling fluidized bed (BFB) boiler for energy production. During the sampling period, when the bottom ash was sampled from the outlet of the boiler and the fly ash from the electrostatic precipitator (ESP) from the boiler, approximately 40 % of the energy produced by the boiler originated from the incineration of commercial peat fuel, and approximately 60 % from the incineration of clean forest residues (*i. e.* bark, woodchips and sawdust). These forest residues originated from the wood handling plant, sawmill, packaging pallet plant and groundwood mill of the pulp and paper mill complex investigated in this study [10], and they were therefore clean residues. Sampling of the ashes was carried out over a period of three days, and the individual samples (1 kg per sampling day) were combined to give one composite sample with a mass of 3 kg for both the bottom ash and fly ash. The sampling period represented normal process operating conditions for the combustion plant, *e. g.* in terms

of O_2 content and temperature. The incineration temperature in a bubbling fluidized bed boiler is ca. 850 °C and the temperature reaches between 1100 and 1200 °C in the upper zone of the boiler, while in the electrostatic precipitator it is ca. 144 °C [11]. After sampling, the samples were stored in plastic bags in a refrigerator (+4 °C). A coning and quartering method [12] was repeatedly applied to reduce the ash sample to a size suitable for conducting laboratory analyses.

Determination of the mineral composition, pH value, dry matter content and neutralizing value in ashes

To determine the mineralogical composition of the bottom ash and fly ash, X-ray diffractograms of powdered samples were obtained with a Siemens D 5000 diffractometer (Siemens AG, Karlsruhe, Germany) using CuK_α radiation. The scan was run from 2 to 80° (2-theta scale), with increments of 0.02° and a counting time of 1.0 s per step. The operating conditions were 40 kV and 40 mA. Peak identification was carried out with the DIFFRACplus BASIC Evaluation Package PDFMaint 12 (Bruker axs, Germany) and ICDD PDF-2 Release 2006 software package (Pennsylvania, USA). The pH of the ashes was determined using a pH/EC analyser equipped with a Thermo Orion Sure Flow pH electrode (Turnhout, Belgium). The determination of pH was carried out according to European standard SFS-EN 12880 at a solid-to-liquid (*i. e.* ultrapure H_2O) ratio of 1 : 5. Determination of the dry matter content of the ashes was carried out according to European standard SFS-EN 12880, in which a sample is dried overnight to a constant mass in an oven at 105 °C. The neutralizing (liming effect) value was determined according to European standard SFS-EN 12945. A comprehensive review of the standards, analytical methods and instrumentation is presented in our previous paper [11].

Determination of the total chloride and water soluble phosphorous concentrations of the ashes

Determination of the total chloride concentration in the ashes was carried out according to European standard CEN/TS 15289 [13]. In this procedure, the ash is extracted with HNO_3

in a CEM Mars 5 microprocessor-controlled microwave oven with CEM HP 500 Teflon vessels (CEM Corp., Matthews, USA) at 120 °C for 1 h. The concentration of chloride in the extract was determined with a Dionex DX500 ion chromatography system (Dionex Corp., USA). Before the nutrient determination, samples were dried overnight to constant mass at 105 °C in a drying oven (Termaks) according to European standard SFS-EN 12880. A more comprehensive review of the standards, analytical methods and instrumentation is provided in our previous paper [14]. Determination of the water soluble phosphorous concentration in the ashes was carried out according to European standard CEN/TS 15105 [15]. In this procedure, the ash is heated with water in a closed container at 120 °C for 1 h. The concentration of phosphorous in the extract was determined with a Thermo Fisher Scientific iCAP6500 Duo (UK) inductively coupled plasma optical emission spectrometer (ICP-OES).

Determination of the total Ca, Mg, K and P concentrations in the ashes

Determination of the total Ca, Mg, K and P concentrations in the ashes was carried out according to ASTM method C 1301-95 [16]. In this procedure, the ash sample is digested by lithium tetraborate ($Li_2B_4O_7$) fusion followed by dissolution in 65 % HNO_3. The cooled solution was transferred to a 100 mL volumetric flask and the solution was diluted to the volume with ultrapure water. The ultrapure water was generated by an Elgastat Prima reverse osmosis and Elgastat Maxima ion exchange water purification system (Elga Ltd; Bucks, England). All reagents and acids were suprapure or pro analysis quality. The Ca, Mg, K and P concentrations in ashes were determined with a Thermo Fisher Scientific iCAP6500 Duo ICP-OES (UK). A more comprehensive review of the standards, analytical methods and instrumentation is provided in our previous paper [17].

Determination of the total heavy metal concentrations in the ashes

To determine the total heavy metal concentrations (B, As, Cd, Cr, Cu, Hg, Pb, Ni and

Zn) in the ashes, the dried sample was digested with a mixture of HCl (3 mL) and HNO$_3$ (9 mL) in a CEM Mars 5 microprocessor-controlled microwave oven with a CEM HP 500 Teflon vessels (CEM Corp., Matthews, USA) using USEPA method 3051A [18]. The cooled solution was transferred to a 100 mL volumetric flask and the solution was diluted to the volume with ultrapure water. The ultrapure water was generated by an Elgastat Prima reverse osmosis and Elgastat Maxima ion exchange water purification system (Elga Ltd; Bucks, England). All reagents and acids were suprapure or pro analysis quality. Except for Hg, the total heavy metal concentrations in ashes were determined with a Thermo Fisher Scientific iCAP6500 Duo ICP-OES (UK). The concentra-

tion of Hg in the ash was determined with a Perkin Elmer Analyst 700 cold-vapour AAS equipped with a Perkin Elmer FIAS 400 and AS 90 plus auto-sampler.

RESULTS AND DISCUSSION

XRD spectra of ash samples are shown in Fig. 1. A Cu-tube was used in the measurement of the XRD spectra, which energizes the X-rays of Fe in the ash. Therefore, the background of the XRD spectra in the figures is relatively high. According to the XRD spectra in Fig. 1, *a*, *b*, the oxide mineral lime (CaO) and phosphate mineral brushite (CaHPO$_4 \cdot$ 2H$_2$O) were the only minerals that existed in both the
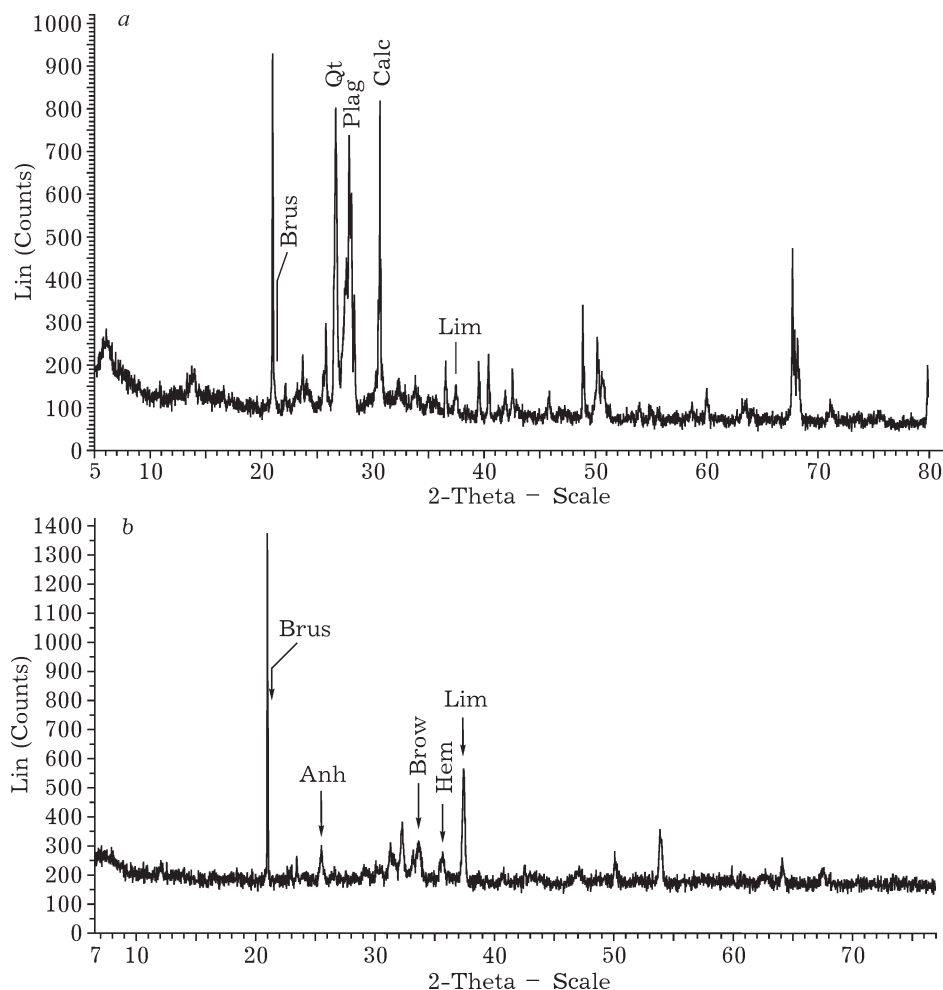

Fig. 1. XRD pattern for the bottom ash (*a*) and fly ash (*b*). Mineral abbreviations and their abundances (%) are: *a* − Brus = brushite [CaHPO$_4 \cdot$ 2H$_2$O; 5.2 %]; Calc = Calcite [CaCO$_3$; 18.5 %]; Lim = lime [CaO; 1.1 %]; Plag = plagioclase (labradorite) [Ca$_{(50-70\ \%)}$Na$_{(50-30\ \%)}$(Al,Si)AlSi$_2$O$_8$; 49.7 %]; Qt = quartz [SiO$_2$; 25.5 %]; *b* − Anh = andydrite [CaSO$_4$; 24.7 %]; Brow = brownmillerite [Ca$_2$FeAlO$_5$; 15.6 %]; Brus = brushite [CaHPO$_4 \cdot$ 2H$_2$O; 19.1 %]; Hemi = hematite (haematite) [Fe$_2$O$_3$; 13.0 %]; Lim = lime [CaO; 27.6 %].

TABLE 1

Physical and chemical properties of the bottom ash and fly ash, as well as the enrichment factors (EF) of elements

Parameter/metal	Unit	Bottom ash	Fly ash	EF	Limit value
pH		11.9	12.6		
Dry matter content (105 °C)	%	>99.5	>99.5		
Neutralizing value (NV)	% (Ca; d.w.)	6.9	26.4	3.8	
Cl	% (d.w.)	<0.01	0.2	(>20)	2.0 (max)
Ca	% (d.w.)	5.8	26.9	4.6	6.0 (min)
Mg	% (d.w.)	0.7	2.3	3.3	
P	% (d.w.)	0.2	1.3	7.5	
K	% (d.w.)	2.6	1.5	0.6	
P + K	% (d.w.)	2.8	2.8	1.0	1.0 (min)
P(H_2O)	% (d.w.)	<0.01	<0.01		
B	mg/kg (d.w.)	84	190	2.3	
As	mg/kg (d.w.)	5	24	4.8	30 (max)
Cd	mg/kg (d.w.)	<0.3	3.2	(11)	17.5 (max)
Cr	mg/kg (d.w.)	23	100	4.3	300 (max)
Cu	mg/kg (d.w.)	16	120	7.5	700 (max)
Hg	mg/kg (d.w.)	<0.04	0.25	(>6.3)	1.0 (max)
Pb	mg/kg (d.w.)	3.0	34	11.3	150 (max)
Ni	mg/kg (d.w.)	13	79	6.1	150 (max)
Zn	mg/kg (d.w.)	380	800	2.1	4500 (max)

Notes. 1. If the total concentration of a compound does not fulfil the requirement for its minimum or maximum limit value, it is presented in a bold type. 2. EF = [total parameter value or element concentration in the fly ash] / [total parameter value or element concentration in the bottom ash].

bottom ash and fly ash. Plagioclase ($Ca_{(50-70\%)}Na_{(50-30\%)}(Al,Si)AlSi_2O_8$) and quartz ($SiO_2$), which both are silicate minerals, as well as calcite ($CaCO_3$), which is a carbonate mineral, only existed in the bottom ash. Anhydrite ($CaSO_4$), which is a sulphate mineral, as well as brownmillerite (Ca_2FeAlO_5) and hematite (Fe_2O_3), also known as hematite, which both are oxide minerals, only existed in the fly ash. Except for brushite and brownmillerite, the XRD data of our ashes agree with the findings of Holmberg and Claesson [19], who observed the same minerals in wood ash as we did in this study.

According to van Herck and Vandecasteele [20], the alkaline pH of the ash indicates that part of the dissolved metals occur as basic metal salts, oxides, hydroxides and/or carbonates, although hydroxides were not observed in our ashes. Thus, the strongly alkaline pH value of 11.9 (bottom ash) and 12.6 (fly ash) in our ashes (Table 1), as well as the minerals in them (see Fig. 1), support the findings reported by van Herck and Vandecasteele [20], although we did

not observe any hydroxides in the ashes. The existence of silicate minerals in the ashes originating from the bubbling fluidized bed boiler is reasonable when considering that the bed material of a fluidized bed boiler usually consists of silica sand. Furthermore, the existence of silicate minerals in these ash fractions may also be partly due to sand and soil particle contamination of forest residues during harvesting, transportation and handling [21]. In addition, it may partly derive from the decomposition of plant tissue-derived Si-based minerals during incineration, such as phytolith ($SiO_2 \cdot nH_2O$), which is often a structural component of plant tissues, deposited between and within plant cells [22]. The dry matter content of the bottom ash and fly ash was very high (>99.5 %). This is a disadvantage, as it may increase the amount of dust generated during the handling of these residues.

Table 1 presents the most relevant physical and chemical properties of the bottom ash and fly ash, as well as the enrichment factors (EF)

for each element. The EF value is determined as the ratio of element concentrations in the fly ash to those in the bottom ash. In cases where the concentration of a particular element in ashes was lower than the limit of detection, the EF value in Table 1 is given in parentheses. An elevated EF value indicates a high degree of element volatilization, whereas a low EF value is indicative of non-volatile behaviour under normal operating conditions and the formation of a heavier mineral phase [23]. In addition to the element volatilization characteristics, element retention in fly ash through other processes (*i.e.* primarily the condensation process) determines the final fate of volatile elements. Most of these species form compounds that condense on the surface of particles in the flue gas, leading to the enrichment of some elements in the fly ash fraction. This phenomenon is well known and depends on many factors such as the type of boiler, the fuel mix, tree species, soil type and climate, and the efficiency of flue gas cleaning devices, and has been reported elsewhere [24−27]. Therefore, we did not focus on this in the present study. However, in this context it is worth noting that the potassium content in the bottom ash was higher (2.8 %; d.w.) than that in the fly ash (1.5 %; d.w.). This contradicts with the findings of Steenari and Lindqvist [21, 23], who reported that potassium is rather easily volatilizable during combustion and is consequently enriched in the fly ash.

The acid neutralizing value (NV) is one of the most important indices in evaluating the liming effect value of the ash in relation to its use in forestry [28]. The capacity of a liming agent to neutralize soil acidity depends on the levels of soluble and hydrolysable bases such as oxides, hydroxides, carbonates and silicates. Cations such as calcium, magnesium, and potassium are the interactive counter-ions. According to the NV values in Table 1, the fly ash has a ca. 3.8 times higher capacity as a liming agent to neutralize soil acidity and act as a soil amendment agent than the bottom ash. This is because the Ca concentration (26.9 %, d.w.) in the fly ash was ca. 4.6 times higher than that in the bottom ash. The NV of 26.9 % (d.w.) for the fly ash indicates that ca. 1.4 t of this residue would be required to replace 1 t of a commercially ground limestone product produced by SMA Mineral Ltd., the neutralizing value of which is 38 % (Ca equivalents; d.w.). In the bottom ash, the respective NV values was 6.9 % Ca (d.w.), indicating that ca. 5.5 t of these ashes would correspondingly be required to replace 1 tonne of the above-mentioned limestone product. The Mg concentration of the fly ash also indicates that it is a better forest fertilizer than the bottom ash. The Mg concentration in the fly ash was ca. 3.2 times higher than that in the bottom ash. However, there were no differences between the bottom ash and fly ash in the P + K concentration or in the water soluble phosphorous concentration. The chloride content in both ash fractions was clearly lower than the maximum limit value (2.0 %; d.w.), although it was higher in the fly ash (0.2 %; d.w.) than that in the bottom ash (<0.01 %; d.w.). As a consequence of the Ca and Mg concentrations, which are of great interest for the utilization of biomass ashes in forests [29], the fly ash is a better plant nutrient and soil improvement agent that the bottom ash. In this context, it is notable that the Ca concentration of 5.8 % (d.w.) in the bottom ash was lower than the minimum limit value of 6.0 % (d.w.) for Ca. Therefore, this residue may not be used as a forest fertilizer without the addition of auxiliary Ca.

Compared to the total phosphorous content, *i. e.* 0.2 % (d.w.) in the bottom ash and 1.3 % (d.w.) in the fly ash, the water soluble phosphorous content in both ashes was negligible (<0.01 %; d.w.). We have also observed the low solubility of phosphorous in wood ash and in the ash originating from the incineration of a mixture of wood-based residues and peat in our previous studies [30, 31], and it has additionally been reported by other researchers [24, 32−34]. According to Demeyer *et al.* [33], the low solubility of phosphorous is most likely because in wood ash it is occluded in alumina-silicates or in the form of weakly soluble aluminium phosphate. However, according to Steenari and Lindqvist [23], this results from the phosphorous in wood ash being present in apatites ($Ca_5(PO_4)_3(F,Cl,OH)$) and other calcium phosphates. Our mineral data from XRD spectra only support the existence of calcium phosphates in the form of brushite ($CaHPO_4 \cdot 2H_2O$) in the bottom ash and fly ash (see Fig. 1). According to Table 1, there are no minimum or maximum

limit values for the dry matter content (DMC), neutralizing value (NV), magnesium (Mg), water soluble phosphorous $P(H_2O)$ or boron (B) in ashes used as a forest fertilizer. However, their content has to be reported to the environmental authorities when ash is used for such a purpose.

In Finland, national legislation regulates the utilization of ash in forestry. The Fertilizer Product Act [14], the Decree on Fertilizer Products [14] and the Decree on the Operations Concerning Fertilizer Products and their Supervision [14] set guidelines for ash recycling and fertilizer use in forestry. At present, only wood, peat or agrobiomass ash is permitted to be used as a raw material for forest fertilizer. In addition, the maximum allowable concentrations are currently only set for As, Cd, Cr, Cu, Hg, Pb, Ni and Zn. According to the results in Table 1, the concentrations of heavy metals (As, Cd, Cr, Cu, Hg, Pb, Ni and Zn) in the bottom ash and fly ash were clearly lower that their limit values and do not restrict the utilization of these residues as a forest fertilizer.

CONCLUSION

Except for potassium with an enrichment factor (EF) of 0.6, other nutrients (Ca, Mg and P), boron (EF = 2.3) and heavy metals (As, Cd, Cr, Cu, Hg, Pb, Ni and Zn) were enriched in the fly ash. The concentrations of As, Cd, Cr, Cu, Hg, Pb, Ni and Zn in the bottom ash and fly ash were lower than their limit values for forest fertilizer. Therefore, both ash fractions are potential forest fertilizers as such. However, due to the total Ca concentration of 5.8 % (d.w.) in the bottom ash, which was lower than the minimum limit value of 6.0 % (d.w.) for Ca, additional Ca is needed if this residue is to be used as a forest fertilizer. Compared to the total phosphorous content, *i. e.* 0.2 % (d.w.) in the bottom ash and 1.3 % (d.w.) in the fly ash, the water soluble phosphorous content in both ashes was negligible (<0.01 %; d.w.). The mineral data in XRD spectra support the existence of calcium phosphates in the form of brushite $(CaHPO_4 \cdot 2H_2O)$ in the bottom ash and fly ash.

Acknowledgements

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